Equivalent formulations of the generalized pericyclic selection rules[1]

There are two distinct sets of criteria,[2] both commonly referred to as the generalized pericyclic selection rules (or generalized Woodward–Hoffmann rules), for determining whether a pericyclic reaction (of any class) is allowed or forbidden. On casual inspection, it is not obvious that these formulations of the generalized pericyclic selection rules are equivalent in the sense that they must reach the same conclusion for every conceivable pericyclic process. Here, we present a rigorous demonstration of this equivalence by introducing a formalism to convert the original statement of equivalence, expressed in chemical terms, to a purely arithmetic proposition, the proof of which is straightforward.

Proposition 1. *The following formulations of the generalized pericyclic selection rules are equivalent:*

A: ('Componentwise') A pericyclic process under thermal conditions is allowed if and only if the sum of the number of suprafacial $4q+2$ *components and antarafacial* $4r$ *components is odd.*

B: ('Global') A pericyclic process under thermal conditions is allowed if and only if the total electron count is $4n+2$ *and the number of antarafacial components is even or the total electron count is* $4n$ *and the number of antarafacial components is odd.*

Proof. We will see that Proposition 1 is equivalent to Proposition 2, whose proof is given below. □

We begin by defining a set of symbols that encode the electron count and the orbital interaction topology of each component in a way that tracks and preserves parity (oddness/evenness). In particular, we assign a k-component pericyclic reaction a set of ordered triples $\{(n_1, f_1, 1), \dots, (n_k, f_k, k)\}$ by associating component i with the triple (n_i, f_i, i) according to the following rules:

$$n_i = \begin{cases} 2r & \text{if } i \text{ is a } 4r \text{ component} \\ 2q+1 & \text{if } i \text{ is a } 4q+2 \text{ component,} \end{cases}$$

and

$$f_i = \begin{cases} 0 & \text{if } i \text{ is suprafacial} \\ 1 & \text{if } i \text{ is antarafacial.} \end{cases}$$

Examples:

(1) The conrotatory ring closing of 1,3,5,7-octatetraene ($_\pi 8_a$) is associated with $\{(4,1,1)\}$.

(2) The conrotatory ring opening of cyclobutene ($_\sigma 2_a + {}_\pi 2_s$) is associated with $\{(1,1,1),(1,0,2)\}$.

(3) The Diels−Alder reaction ($_\pi 2_s + {}_\pi 4_s$) is associated with $\{(1,0,1),(2,0,2)\}$.

(4) The Alder ene reaction ($_\pi 2_s + {}_\sigma 2_s + {}_\pi 2_s$) is associated with $\{(1,0,1),(1,0,2),(1,0,3)\}$.

(Note that the i's are merely labels used to keep track of components. The value of i assigned to a given component is arbitrary.)

We can restate the condition in the 'componentwise' formulation (A) as "if the number of components of the form $(2q+1,0,i)$ or $(2r,1,i)$ is odd," or, since $n_i + f_i = 2q+1$ or $2r+1$ is odd for (only) these components, as "if the number of components with the property that $n_i + f_i$ is an odd number is odd." To restate the 'global' formulation (B), we first observe that the total electron count of the pericyclic reaction is $2\sum_i n_i$, where $\sum_i$ indicates a sum from $i=1$ to $i=k$. So the total electron count is $4n+2$ or $4n$ if $\sum_i n_i$ is odd or even, respectively. On the other hand, the total number of antarafacial components is $\sum_i f_i$. Thus we can restate the condition in formulation B as "if $\sum_i n_i$ is odd and $\sum_i f_i$ is even or vice versa." The following is then equivalent to Proposition 1 in our new notation:

Proposition 2. *Let* $S = \{(n_1, f_1, 1), \dots, (n_k, f_k, k)\}$ *be a set of ordered triples with* $n_i \in \{0,1,2,\dots\}$ *and* $f_i \in \{0,1\}$*, and let* $T = \{(n_i, f_i, i) \in S \mid n_i + f_i \text{ is odd}\}$*. Then* $|T|$ *is odd if and only if exactly one of* $\sum_i n_i$ *and* $\sum_i f_i$ *is odd.*

Proof. Since exactly one of $\sum_i n_i$ and $\sum_i f_i$ is odd if and only if $\sum_i n_i + f_i$ is odd, we only need to show that $|T|$ is odd if and only if $\sum_i n_i + f_i$ is odd. This statement is true by inspection because the sum of a sequence of integers is odd if and only if there are an odd number of odd terms in the sequence. More explicitly, we note that any ordered triple in S such that $n_i + f_i$ is even can be omitted from the sum of the $n_i + f_i$ without a change in parity, since $n_i + f_i \equiv 0 \pmod 2$ for such ordered triples. In other words, $\sum_i n_i + f_i \equiv \sum_T n_i + f_i \pmod 2$, where $\sum_T$ indicates taking the sum over all i such that component i is in T. But $n_i + f_i \equiv 1 \pmod 2$ for ordered triples in T, so $\sum_T n_i + f_i \equiv \sum_T 1 = |T| \pmod 2$. Thus $|T| \equiv \sum_i n_i + f_i \pmod 2$, i.e., they have the same parity, as claimed. □

[1] Y.-M. Wang, revised 3-Jan-2026.

[2] The 'componentwise' formulation was proposed by Woodward and Hoffmann in *ACIEE* **1969**, *8*, 781. Because the number of antarafacial components and the number of phase inversions (for any choice of basis orbitals) have the same parity, the 'global' formulation can be regarded as a reframing of the Dewar–Zimmerman aromatic transition state theory (Hückel vs. Möbius topology) using Woodward–Hoffmann terminology; see *JACS* **1966**, *88*, 1563; *Tetrahedron* **1966**, *Suppl. 8*, 75.